TECHNICAL REPORT

72-55-FL

IRRADIATION INDUCED HEADSPACE GASES IN PACKAGED RADIATION STERILIZED FOOD

by

George B. Pratt

and

Lloyd E. Kneeland

American Can Company

Barrington, Illinois

Contract No. DA19-129-AMC-119(N)

February 1972

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UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

U.S. ARMY MATERIEL COMMAND

Food Laboratory

FL-158

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13. ABSTRACT

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The following techniques were found to mitigate the effects of gas production:

1. Use of recommended fill of container and closing vacuum effectively prevent swelled containers. Disadvantage: slightly reduced fills are entailed for meat.

2. Vacuum sealing <u>after</u> irradiation using clinched cover technique reduced headspace gas. Disadvantages: slightly reduced fills as well as danger of recontamination.

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Irradiated Foods	9		9		9	
Radiation Sterilization	10					
Packaging			8			
Sealing			10			
Vacuum Sealing			10			
Irradiation Temperature			6			
Analysis					8	
Induced	0				0	
Mathematical Model					10	
Gas Production					4	
Estimating					4	

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13. Abstract (continued):

3. Plastic window cans permitted hydrogen rapidly to diffuse out thereby creating a vacuum. Disadvantage: some oxygen diffuses into the package albeit slowly.

4. Palladium catalyst reduced headspace gas volume by catalyzing oxidation of hydrogen produced by irradiation. Disadvantage: entails presence of oxygen.

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Lloyd E. Kneeland

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FOREWORD

The availability of shelf-stable, highly acceptable meat items for use in military feeding systems is considered a necessity. The currently available thermally processed items do not fully meet requirements because of their limited utility, stability and acceptability. Radiation processing, or "cold" sterilization as it is frequently called, has the potentiality of yielding products that have good military utility, good storage stability, and good acceptability. Therefore, research to develop process criteria that can be used to produce irradiation sterilized meats is underway.

The work covered in this report was performed by American Can Company Research Laboratories, Barrington, Illinois, under Contract DA19-129-AMC-119(N) during the period from 26 June 1963 to 9 September 1966. It presents the results of a series of investigations on the influence of the radappertization process on induced headspace gases from the sterilized foods. Experiments were conducted to identify the gases, to determine their origin and to develop techniques for their control. The investigation was performed under Project No. 7X84-01-002, Radiation Preservation of Food.

Mr. G. B. Pratt was the Project Officer and Official Investigator and L. E. Kneeland the Collaborator in the research work for American Can Company. The U. S. Army Natick Laboratories Project Officer was Dr. F. Heiligman of the Food Laboratory and the Alternate Project Officer was Mr. J. J. Killoran of the General Equipment and Packaging Laboratory.

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ABSTRACT

A series of studies were conducted to determine the influence of radappertization on induced headspace gases from the sterilized foods. Experiments were performed to identify the gases, determine their origin and develop techniques for their control. Hydrogen gas is the dominant gas produced by the radiation process. Other gases, such as CH_4, CO and CO_2, may also be present in small amounts. In Model systems, the amount of induced gas was found to vary directly with irradiation dose, and to a lesser extent with the concentration of particular food components. Gas production varies inversely with pH. In a study of packaging materials, tinplate and glass had no effect on the type or quantity of gas produced. Packaging in a polyolefin plastic material caused a small increase in H_2. Product temperature during irradiation has a pronounced effect on gas production: approximately half as much as was produced by irradiation at temperatures below 0^oC as by irradiation above this temperature. Type of radiation (cathode vs. gamma), initial can vacuum, or extended periods of storage had no effect on amount of gas produced. A mathematical model for estimating the production of induced gases from proximate analysis successfully predicted gas productions in the five food products investigated.

The following techniques were found to mitigate the effects of gas production:

1. Use of recommended fill of container and closing vacuum effectively prevent swelled containers. Disadvantage: slightly reduced fills of containers.

2. Vacuum sealing <u>after</u> irradiation using clinched cover technique reduced headspace gas. Disadvantages: slightly reduced fills as well as danger of recontamination.

3. Plastic window cans permitted hydrogen to diffuse out rapidly thereby creating a vacuum. Disadvantage: some oxygen diffuses into the package, albeit slowly.

4. Palladium catalyst reduced headspace gas volume by catalyzing oxidation of hydrogen produced by irradiation. Disadvantage: entails presence of oxygen.

INTRODUCTION

Gas produced during high level irradiation of canned food may result in bulged or swelled cans as had been previously reported (Pratt, 1955, 1960). Since users of canned food will normally interpret a swelled can as a sign of bacterial spoilage, there is real concern over this condition.

That the problem of gas production is not confined to products in cans is suggested by Hannan's (1956) report of gas production in unpackaged irradiated fruit. The production of gas on irradiation of food constituents has been the subject of considerable fundamental research in recent years (Dilli and Garnet, 1963; Phillips and Baugh, 1963).

The work reported herein is divided into two phases:

Phase I was designed to explore the problem of radiation induced gases in the context of potential commercial application.

Phase II was designed to find solutions to the problem of cans swelled by irradiation induced gases.

Experimental Method - Phase I.

A. Analytical procedures

Using a Burrel K-1 Chromatograph, a molecular sieve 13x column was used to separate H_2, O_2, CO and CH_4. CO_2 was measured by absorption in a 50% KOH column. H_2S was determined using a 2-meter column packed with tricresyl phosphate on firebrick. Amines, though not expected because of the acid nature of the products, were checked using a diatomaceous earth column impregnated with Teflon and treated with Carbowax 550.

Using the method of water displacement the headspace gas was removed from the various irradiated packaged foods, measured volumetrically and finally analyzed according to the procedure described above.

B. Examination of stored products

Samples of chili, cherries, green beans, beef, and bacon in various packages, some as old as seven years from previously reported studies (Pratt, 1955, 1960), were recovered from storage and headspace gas measured and analyzed as described above. Since no unirradiated controls for these samples were available for comparison, gas analysis must be regarded as qualitative rather than quantitative.

C. Preparation of irradiated test packs

1. Food components. Model systems, representing the major food components--water, fat, protein and carbohydrate--were prepared to determine the types and quantities of gas produced by each on exposure to sterilizing doses of irradiation.

Carbohydrates represented by sucrose, dextrose and starch; protein represented by gelatin; and fat represented by corn oil, were packed both dry and as water solutions in 303 x 406 (1-lb) unlined cans. The dry materials were closed under full line vacuum (about 28 inches Hg) on a No. 1 Pacific closing machine to eliminate air as completely as possible. The water solutions were hot-filled into cans at 93°C and closed on a Canco 006 closing machine with steam flow to exclude headspace air. After closing, the cans packed with sucrose, dextrose, distilled water and water + salt (N_aCl) solutions were held inverted for at least five minutes to sterilize the headspace. The cans containing starch, gelatin and oil solutions were pressure processed for thirty minutes at 115°C to prevent bacterial spoilage.

Samples of all model systems were shipped to Natick where they received 4.5 Mrad gamma irradiation dose from a cobalt-60 source. Doses, as stated in this report, are minimum doses and may range up to 120% of the minimum dose.

2. Irradiation temperature. Unless otherwise specified the irradiation was done without temperature control with product temperature ranging from 4°C up to 26°C and is termed "ambient" temperature irradiation. An experiment to determine the effect of irradiation temperature on gas production utilized sucrose and gelatin solutions packed in 303 x 406 cans. Packing and irradiation procedures were the same as described in the previous experiment except that the samples were irradiated at five different temperature levels ranging from 20° to -196°C.

3. Packaging materials. Sucrose solution (25%) was used in this experiment to determine the effects of packaging materials on irradiation induced gases. Glass packaged samples were prepared by filling 60 ml of hot sucrose solution at 93°C into 100-ml volumetric flasks and heat-sealing the neck of the flasks while under full vacuum (28 in. Hg). Scotch-Pak plastic pouches were filled with 60 ml of hot sucrose solution then heat sealed through the liquid to eliminate air. The pouches were then placed in 202 x 204 cans and closed under full vacuum (28 in. Hg).

Tinplate packed samples were prepared by hot filling 60 ml of sucrose solution into 202 x 204 cans and closing at atmospheric

pressure. After cooling, the cans were punctured then resealed under full line vacuum using a solder-tipping device. All samples were irradiated at 4.5 Mrads at ambient temperatures.

4. Food component concentration and irradiation dosage. Sucrose and gelatin solutions each prepared at three concentration levels were packed in 303 x 406 (1-lb) cans, using the same packing techniques as described previously. Each solution variable was then divided into four equal sets of samples and each set exposed to four irradiation dose levels: 0, 2, 4, and 8 Mrad.

The three sucrose solutions were 1, 5, and 25%, and the gelatin solutions 1, 6, and 12%.

5. Interaction of food components. For the purposes of this experiment, two synthetic food systems were prepared representing a high protein and a high carbohydrate food respectively. The compositions of the systems were as follows:

High-carbohydrate system	High-protein system
1% gelatin	10% gelatin
8% sugar	1% sugar
1% salt	1% salt
90% water	7% fat
	81% water

Both formulations were hot filled at 93°C into 303 x 406 (1-lb) cans, closed with steam flow and pressure processed for 30 minutes at 115°C. At Natick the packed samples were exposed to 4.5 Mrads gamma irradiation at ambient temperatures.

6. Irradiation induced gas in various meat products. In a series of experiments conducted at Natick the following packs were prepared and 12 cans of each product exposed to 4.5 Mrads gamma irradiation at 2°C. An additional 12 cans each of beef and chicken breasts were irradiated near liquid nitrogen temperature, about -185°C.

Non-irradiated controls of each product were prepared in the same manner as described above, except the cans were frozen at -29°C after sealing.

(a) Beef

Commercial grade boneless beef loins were trimmed, stuffed into plastic casings and steam heated at 104°C to a center temperature of 74°C to inactivate enzymes. The beef was then removed from the casings, filled hot into 401 x 209 cans (approximately 12 ounces per can) and closed under 20 inches vacuum.

Prior to irradiation the cans were refrigerated at 2°C.

(b) Pork

Boneless loins, U. S. Grade No. 1 were prepared in the same manner as the beef loins.

(c) Ham

Boneless rolled smoked hams with no special enzyme inactivation were trimmed and filled cold at 4°C into 401 x 209 cans and closed under a vacuum of 20 inches Hg.

(d) Chicken Breasts

Fresh market chicken breasts without bones were steam heated at 140°C to an internal temperature of 79°C to inactivate enzymes and packed as described under beef.

(e) Chicken Thighs

Fresh market chicken thighs with the bones left in were packed as described under chicken breasts.

7. Closing Vacuum. Chicken breasts without bones were packed into 404 x 700 size cans as described above (Paragraph C 6 (d)) and closed under mechanical vacuum at four levels of vacuum at U. S. Army Natick Laboratories. These were subjected to 4.5 Mrads and headspace gas analyzed at 0, 6 and 12 month storage.

8. Acidity. In an experiment to study the effects of pH on gas production, the test media was 6% sucrose solution. Using appropriate amounts of citric acid and disodium phosphate, three solutions were prepared having pH values of 4.0, 5.5 and 6.8 respectively. Eight cans of each solution were packed in 303 x 406 cans and subsequently irradiated at Natick with a dosage of 4.5 Mrads.

9. Radiation Source. Samples of beef in laminated flexible packages which had been subjected to 4.5 Mrads gamma radiation at three temperature levels were received from U. S. Army Natick Laboratories for comparison with similar samples subjected to electron beam irradiation at similar dose and temperatures.

10. Storage. In most of the packs described above samples were placed in storage at 22°C (where not otherwise indicated) and gas analysis performed at several periods to determine whether there is an increase in radiation gas with time of storage.

Experimental Method - Phase II

A. General Methods

1. Analytical. The water displacement method was used for the removal and measurement of gas in all test containers. In the case of meat products, compression was applied under water to insure removal of entrapped gas.

The methods of chromatographic gas analysis are described in Phase I of this study.

2. Product examination of bacon in 307 x 509 cans (stored for twenty-one months at 21°C) included organoleptic examination, by an experienced panel, of the bacon baked 10 minutes in a 148°C oven, and a qualitative examination for catalase activity using chilled dilute hydrogen peroxide solution. (Hawk et al. 1947)

3. Bacteriological examination of a can of swelled beef sealed after irradiation involved aseptic opening of the can and microscopic examination of a smear of the contents stained with crystal violet.

B. Exploration of New Techniques

A series of experiments to evaluate several techniques for the mitigation of the effects of irradiation induced gases are described below under appropriate headings.

1. Product fill and closing vacuum control. Knowing the amount of gas produced in a product for a given radiation dose and temperature, it then becomes possible to calculate the fills and closing vacuums necessary to avoid swelling of the container after irradiation.

This is expressed in the following equation:

$$x = \frac{c\,(v_1 - v_2)\,d}{(v_1 - v_2) + Pa\,Gr\,d}$$

where

x = product fill in grams
c = total container capacity in milliliter
v_1 = gauge vacuum in container before irradiation (ins. Hg)
v_2 = gauge vacuum in container after irradiation (ins. Hg)
Pa = atmospheric pressure (ins. Hg)
Gr = volume of radiation gas for a given product, radiation dose and temperature (milliliters per gram)
d = density of the product (gr/ml)

2. Control of gas by vacuum sealing <u>after</u> irradiation, using clinched cover technique.

(a) Bacon

Bacon, packed and irradiated at Natick in 303 x 509 cans, was used for these studies. A total of 72 cans were packed with parchment-wrapped bacon, 36 cans with a 16 oz. and 36 cans with a 20 oz. weight fill. Twelve cans of each fill were sealed under 25 in. Hg vacuum and irradiated at 4.5 Mrads. Another twelve cans of each fill were "clinch closed" (covers loosely clinched to the containers), irradiated at 4.5 Mrads and finally sealed under 25 in. Hg vacuum. The remaining 12 cans of each fill were sealed under 25 in. vacuum and frozen immediately to serve as controls on the irradiated samples.

Further evaluation of the clinched cover technique was provided in a series of test packs conducted at Natick in June, 1965. The products were beef, ham, pork and chicken, prepared as described below.

(b) Beef

Commercial grade boneless loins; trimmed, stuffed in 6M casings - enzyme inactivated in steam at 104°C to a center temperature of 74°C (approximately 90 minutes required).

(c) Pork

Boneless loins, U. S. Grade No. 1; prepared the same as beef.

(d) Ham

Boneless rolled Wilson; no enzyme inactivation required.

(e) Chicken breasts and thighs

Enzyme inactivated in steam at 104°C to internal temperature of 80°C (approximately 18 minutes).

Except for ham, which was cold filled, the above products were hot filled into 401 x 209 cans (approximately 12 oz./can) and closed under 20 in. vacuum, or "clinched" closed. Prior to irradiation the packed cans were refrigerated at 2°C and irradiated at this temperature. Additional cans of beef and chicken breasts were irradiated at near liquid nitrogen temperature approximately -185°C. Following irradiation the "clinched" cover samples were sealed under 20" vacuum.

Non-irradiated controls for each product were prepared by freezing cans immediately after filling and closing under 20 in. Hg. vacuum.

3. Hydrogen Permeable Plastic Window Container.

(a) Mylar Window

An initial exploratory test of this concept was made with 404 x 307 cans having covers incorporating a Mylar plastic window. Twelve cans were filled with dry sucrose and closed under 4 in. Hg. vacuum. Eight of the cans were irradiated at 4.5 Mrads, and the remaining four left unirradiated to serve as controls.

(b) Mylar/Saran Window

A second test utilized 401 x 209 cans incorporating Mylar/Saran laminate windows. Approximately thirty cans were cold 5°C packed with boneless rolled ham, closed at 20 in. Hg vacuum and frozen at -29°C. Twenty-four cans were shipped frozen to Natick for irradiation at 4.5 Mrads; the remaining six held frozen at this laboratory as controls.

4. Palladium Catalyst to Reduce Irradiation Gas.

(a) Dry Sucrose - High Pd

As an initial test, dry sucrose was packed in 303 x 406 cans and closed at atmospheric pressure. Six cans were closed each with one gram of "palladium black" enclosed in a filter paper pouch, and twelve cans were closed without palladium. Six each of the cans with and without palladium were irradiated at 4.5 Mrads, the remaining six cans held unirradiated.

(b) Ham - Low Pd

In a second experiment conducted at Natick, three levels of palladium catalyst were included with ham, cold (2°C) packed in 401 x 209 cans and closed under 20 in. Hg vacuum. Palladium was contained in 0.5 mil polyethylene pouches in the amounts of 0.5 milligrams, 5.0 milligrams and 50 milligrams per pouch. Six cans at each catalyst level including "no catalyst" were packed and irradiated at 4.5 Mrads. An additional six cans each with 0.5 milligrams and no palladium were frozen immediately after packing, and stored at -30°C to serve as controls on the irradiated samples.

(c) Ham in Pd Catalyzed Pouches

A third test involved "Pd catalyzed" flexible pouches having the following laminate structure from the inside out: polyethylene/Pd catalyst/polyethylene/aluminum foil/polyethylene/paper. Pouches were approximately 5" x 5" in overall size. Non-catalyzed pouches supplied by Natick to serve as controls were laminated from inside out as follows: polyethylene/aluminum foil/mylar: overall size 3" x 7". Pouches were packed with 3 oz. av. slices of ham, sealed with and without vacuum, and irradiated (4.5 Mrads) or frozen. Using the non-destructive method of weighing under water at 20°C, the gross volume, net volume and free space (theoretical vacuum) in the pouches can be determined. Thus a comparison between irradiated and non-irradiated (frozen) samples will give a direct measure of the volume of irradiation induced gases.

Similar comparisons can be obtained between catalyzed and non-catalyzed pouches, and between zero and full vacuum sealing. Sample calculations are shown below.

Pouch	Sealing Vac. (in Hg)	Gross Wt in Air (g)	Gross Wt. (g) in Water (20°C)	Gross[1] Vol. of Pouch (ml)	Net[2] Vol. of Pouch (ml)	Vol.[3] of Ham (ml)	Free Space (ml)
Pd catalyzed (Irradiated)	Full	103.0	-2.0	105	100	91	9
Non-catalyzed (Irradiated)	Full	106.0	-3.0	109	105	95	10
Non-catalyzed (Frozen)	Full	105.0	7.5	97.5	93.5	94	-0.5

1. Gross Vol. (cc) = Gr. wt. in air (g) $\left[\dfrac{\text{-Gr. Wt. in } H_2O\text{(g) } (20^{\circ}C)}{\text{Density of water } (20^{\circ}C)}\right]$

2. Net Vol. (ml) = Gr. vol. (ml.) - pouch material vol. (ml)

3. Vol. of Ham = $\dfrac{\text{Wt. of Ham}}{\text{Density of Ham (1.067)}}$

(d) Shrimp in Pd Catalyzed Pouches

A fourth test also involved Pd catalyzed pouches as described above, packed with shrimp at Natick. Six each of catalyzed and non-catalyzed pouches were packed with approximately 2-1/2 oz. of shrimp per pouch, sealed under full (27 - 28 in. Hg) vacuum and irradiated at 4.5 Mrads. No non-irradiated (frozen) controls were provided.

(e) Shrimp in Cans - Very Low Pd

A fifth test of palladium, involved shrimp packed in 401 x 411 cans at Natick. Three cans were packed with 0.5 mg palladium (contained in 0.5 mil polyethylene pouches) and three without. All were packed with 2 packets of activated charcoal, closed under full vacuum and irradiated at 4.5 Mrads.

RESULTS AND DISCUSSION - Phase I

A. Examination of stored products

Table 1 summarizes headspace gas analysis in cans containing irradiated chili, cherries, green beans, beef, and ham, and in plastic bags of irradiated ham. Besides the atmospheric gases N_2 and O_2 which could be due to incomplete evacuation of air, the cans contained CH_4, CO_2, CO, and especially H_2 in appreciable quantities. These gases have been previously reported as produced by irradiation of food components (Mitchell, 1957). The gases NH_3 and H_2S and their analogs, produced by irradiation of amino acid (Weeks and Garrison, 1958; Swallow 1963), were not detectable as components of headspace gas.

The gases observed were obviously influenced by the type of container and the long storage times involved. The absence of H_2 and CO_2, in the plastic packages can be explained by the high degree of permeability of polyethylene to these gases (noted by Brubaker and Kammemeyer, 1953). In the canned samples H_2 produced by corrosion probably contributed to that found in the cans. Enzymatic activity in the beef evidently contributed CO_2 to that found in the cans. This was confirmed in bacon stored 21 months as reported below.

It must be emphasized that these samples were not specifically prepared to study headspace gases but were later (some much later) selected to provide a general survey of the problem.

B. Examination of test packs

Throughout the test packs the same gases reported above (CH_4, CO_2, CO and H_2) were observed while higher hydrocarbons, NH_3, H_2S, and their analogs were not.

1. Food components. Table 2 reports gas produced by representative irradiated food components both dry and mixed with water. Gas analysis of unirradiated controls appears in Table 3.

By far the greatest amount of gas produced was hydrogen. The carbohydrates (sucrose, dextrose, starch) yielded the greatest amount of gas with fat and protein yielding somewhat less. The quantities (ml) of radiation induced gases were greater in the cans of dry products. This would be expected due to the greater concentration of the food component (100%) in the dry pack compared to the water pack (6-10%). Actually the yield of irradiation gas on a per gram of dry product basis was much higher with water packs than dry packs. Where water is present, therefore, radiolysis of water makes an important contribution of hydrogen (Siu and Bailey, 1957).

The volume of hydrogen produced is less than would be predicted using G-values provided by Phillips and Baugh (1963) perhaps because of back reactions due to increasing pressure of reaction products described by Dalton et al. (1963).

2. Radiation temperature.

Table 4 reports total gas in solutions of gelatin and sucrose irradiated at temperatures from -196 to 20°C. Less gas was produced when the product was irradiated at temperatures below the freezing point than above this temperature. The greatly reduced gas production at temperatures below freezing was confirmed with beef and chicken under Phase II below (See Tables 12, 15 and 18).

3. Packaging materials.

Since the problem of gas production during irradiation has been observed only (or primarily) in canned product, the question naturally arises whether the can itself is contributing to gas production.

Table 5 reveals that approximately the same amount of hydrogen is produced in a model system whether packed in glass, in metal, or in plastic. However, statistical analysis reveals that total H_2 in the plastic package is somewhat greater than in the glass (statistically significant at the 1% level). This could be explained by the well known fact that hydrogen gas is produced on irradiation of plastic materials themselves (Tripp, 1957; Killoran, 1967). By the time gas analysis was possible, most of the hydrogen gas had permeated from the inside of the bag to the outside.

As a practical matter hydrogen gas production should be little or no problem with irradiated plastic packaged products because of the very rapid permeation of hydrogen through most plastic films.

4. <u>Irradiation dose and food component concentration.</u>

The gas produced on irradiation of aqueous sucrose solutions of various concentrations appears in Table 6. Similar information for gelatin solutions appears in Table 7. Using a Control Data G-15 computer and least squares techniques, the observed data points were fitted to a simple mathematical model. The six lines appearing in Figure 1 (as well as the data points themselves) are all plotted from the single resulting formula.

$$Y = .40 + 10.27\, x_1\, (1 + .02123\, x_2) \qquad \text{Formula A}$$

Where Y = ml of gas at 4 months
x_1 = dose in Mrad
x_2 = percent sucrose in solution

The data points fit the above mathematical model extremely well (correlation coefficient, $R = 0.992$).

This model provides some hint of the mechanism of gas production. Note that over the range of doses to 8 Mrad the gas production is directly proportional to the radiation dose. The sugar solutions acted almost as dosimeters. Although related to concentration of sucrose, gas production was obviously not proportional to sucrose concentration.

The mathematical model is consistent with the familiar hypothesis (Siu and Bailey, 1957) of water as the principal source of the radiation produced gas (hydrogen, at any rate). Sucrose plays a necessary but secondary role as indicated by the modest differences in gas produced by massive changes in concentration of sucrose. The hypothesis of sucrose as a scavenger of hydroxyl radicals would be consistent with this finding.

The simple model above does not, of course, help explain the presence of CO_2, CO and CH_4, which are produced in small amounts. These gases might be direct products of splitting of sucrose or the oxides might result from oxidation of the sugar.

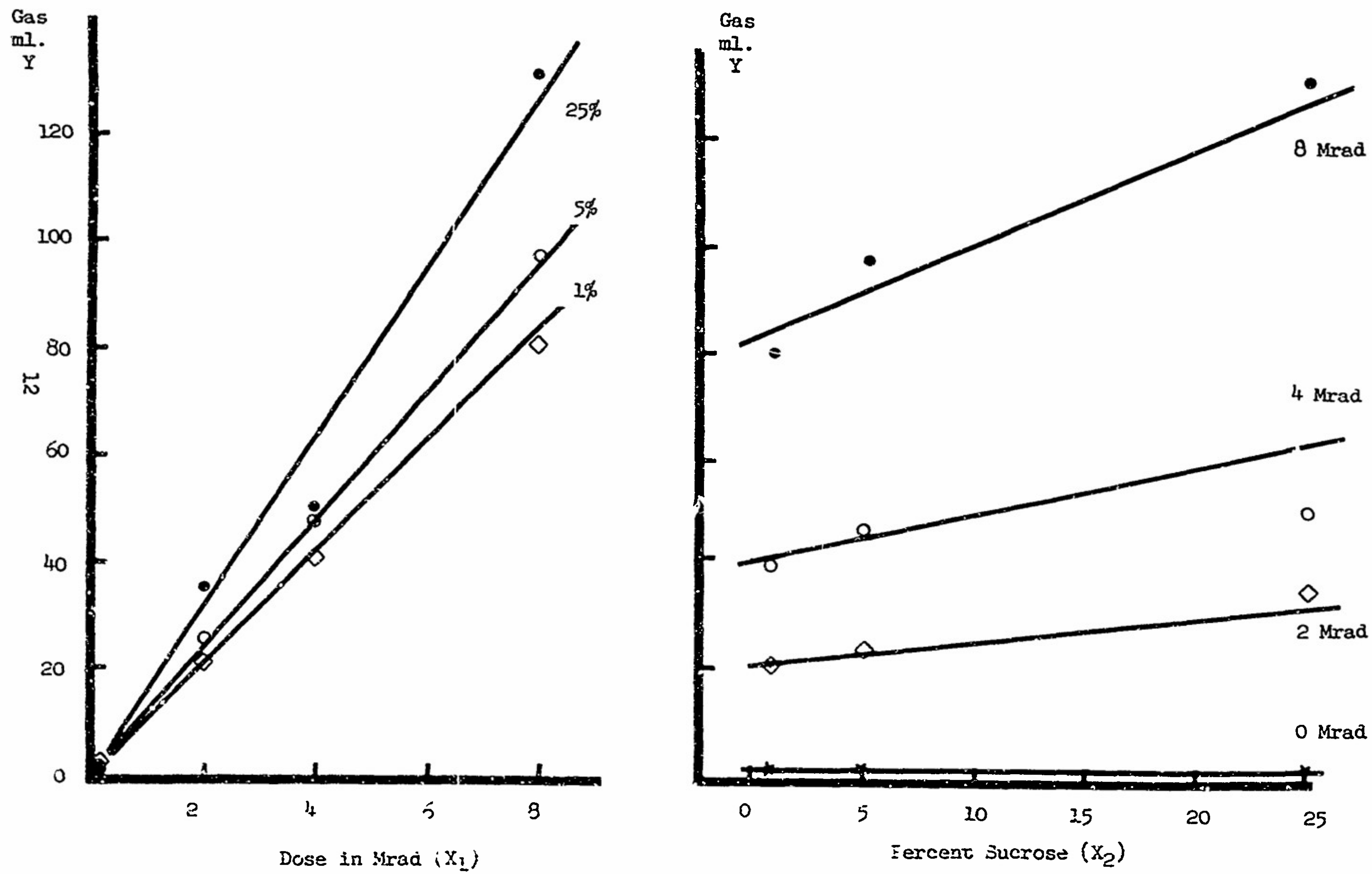
The irradiation of gelatin produced an analogous situation (Table 7 and Figure 2) except that the 1% gelatin variable irradiated at the highest doses produced much less gas than anticipated. This anomaly, associated with the highest doses, which was confirmed on subsequent experiments, may be due to exhausting of the available gelatin before the full dosage is achieved. The computed model for gelatin was found to be:

$$Y = 1.2 + 7.75\, x_1\, (1 + .0154\, x_2) \qquad \text{Formula B}$$

Where Y = ml gas at 4 months
x_1 = dose in Mrad
x_2 = percent gelatin in solution

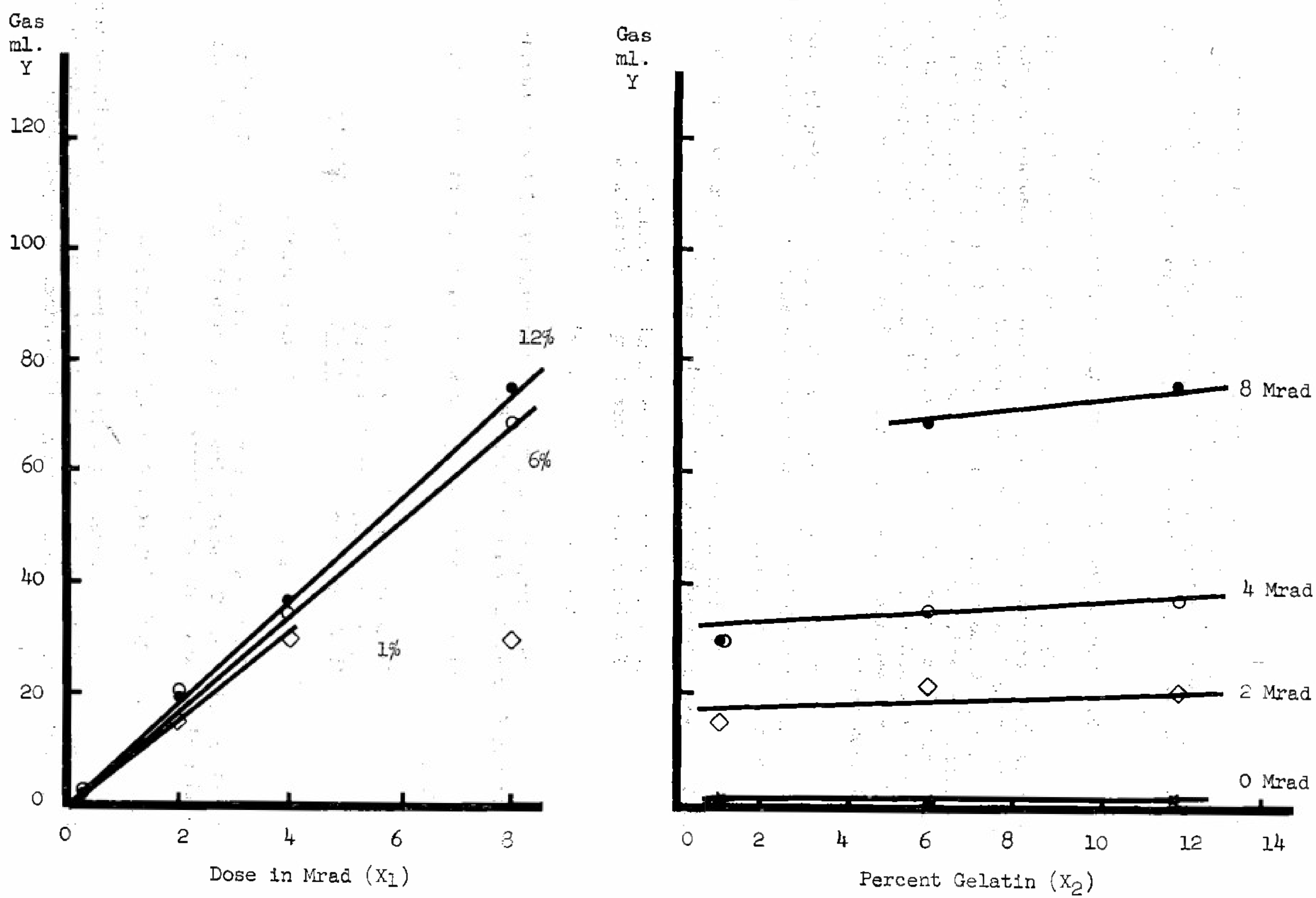
GAS PRODUCED ON IRRADIATION OF SUCROSE

$$Y = .4 + 10.27\,X_1\,(1 + .02123\,X_2)$$



Gas Produced on Irradiation of Gelatin

$$Y = 1.2 + 7.75\,X_1\,(1 + .0154\,X_2)$$



The data points (with the exception noted above) fit this model extremely well (correlation coefficient, R = .999). Of course, these equations should not be extrapolated beyond the bounds of dose or product concentration of the experiment or to greatly higher or lower temperatures.

5. Interaction of food components--simulated foods.

Table 8 presents the detailed gas analysis of two model systems (high carbohydrate and high protein). Of immediate interest was the comparison of irradiated sucrose solutions previously presented in Paragraph 4 above with the model system containing both sucrose and gelatin. The addition of gelatin actually resulted in reduced gas production in sucrose solutions. Obviously, therefore, the effect is not directly additive. The production of gas from a mixed system was in fact intermediate between the amounts of gas produced by the individual components.

The following method involving simple averaging is based on a model for radiolysis of water with non-water molecules competing for the free radicals produced.

Using the equations from Paragraph 4 above, we can predict the gas produced by the high carbohydrate model:

8% sucrose would produce	55 ml	(Formula A)
1% gelatin would produce	25 ml	(Formula B)
Average	40 ml	

The actual gas produced in the mixture of these components was 41.5 ml to 44 ml in Table 8.

As a second example, let us consider the high protein model:

10% gelatin would produce	40 ml	
1% sucrose would produce	45 ml	
7% fat would produce	15 ml	(From Table 2)
Average	33 ml predicted	

The actual gas produced in this mixture was 31.7 ml to 40 ml in Table 8. The predictions agree with the experimental data well within the experimental error.

6. Irradiation-induced gas in meat products.

Table 9 presents gas analyses for packs of irradiated beef, pork, ham, chicken breasts, and chicken thighs and bacon compared with irradiation gas predicted from typical proximate analysis values.

As an example, let us consider the experience with chicken breast in 401 x 209 cans. Proximate analysis of canned boned chicken are from the Canned Food Reference Manual (p. 380, 1947).

Protein	30% would produce	51 ml	(Formula B)
Fat	8% would produce	<u>15 ml</u>	(From Table 2)
No carbohydrate			
Average		33 ml	predicted for 1-lb can; found 30-32 ml.

The chicken thigh was found to be 11% bone. If we assume no gas production from bone, the estimated gas production would be 29 ml for chicken thigh; 23-29 ml was found.

As another example, bacon was calculated as follows:

Protein	8% would produce	40 ml	(Formula B)
Fat	74% would produce	<u>22 ml</u>	(From Table 2 ignoring N_2 and O_2)
No carbohydrate			
Average		31 ml	predicted for 1-lb; found 30-37 ml.

Gas production for the three other products was predicted in an analogous fashion from their proximate analyses.

It appears probable that irradiation-induced gas production for other meat items can be predicted by averaging the expected gas production, for any given radiation dose and temperature for the protein and fat components, based on Proximate Analysis.

7. <u>Closing vacuum</u>.

Table 10 shows gas analysis in 404 x 700 chicken closed at 10, 15, 20, and 25 inch vacuum. About the same amount of irradiation gas (H_2, CO_2, CO and CH_4) was present regardless of closing vacuum. Of course, the higher the vacuum the less atmospheric gas was recovered.

8. <u>Acidity</u>.

Gas analysis of samples of sucrose solution buffered to three pH levels is presented in Table 11.

Gas production is almost directly proportional to hydrogen ion concentration. This is the expected result in view of the fact that the gas produced on irradiation of sugar solution is predominantly hydrogen.

The increase in numberical pH value after irradiation, indicating a depletion of the hydrogen ion in solution, also corresponds to the increased hydrogen production in the buffered solutions.

9. Radiation source.

In the limited samples available, gas analysis presented in Table 12 indicates no difference in gas produced by electron irradiation as compared to gamma radiation at any temperature.

10. Storage.

A very comprehensive number of comparisons of gas measurements made over extended storage periods is available as listed below.

Although some early indications were obtained of a modest increase in gas with storage time, the great bulk of data clearly indicate that there is no consistent increase in radiation gas with storage time even over periods up to 21 months.

Comparisons may be seen in Tables 4, 5, 8, 10, 14, 14a, 15, 16, 17, 18, 19, 20, 21, 22, 23, 25, 26 and 27.

RESULTS AND DISCUSSION - Phase II

A. Results of Exploration of New Techniques for Mitigation of Effects of Radiation Induced Gases.

1. Product fill and closing vacuum control.

Calculations as outlined under experimental method B 1 above indicate that the problem of swelled cans (or low vacuum cans) of meat products can be solved by high can vacuums at the time of closing and sufficient headspace in the cans. Generally speaking less fill can be accommodated than with thermally processed meats.

The recommended fills and estimated vacuum after irradiation presented in Table 13 are calculated values; they were not experimentally determined. In the few size and product combinations where experimental data are available, agreement is good.

Average specific gravity (by immersion) of samples of four boneless irradiated products was found to be as follows:

Product	Specific Gravity
Beef	1.075
Ham	1.067
Chicken	1.00
Bacon	.956

2. Control of gas by vacuum sealing after irradiation using clinched cover technique.

(a) Bacon

Table 14 compares total gas and gas analysis of headspace gas in irradiated bacon vacuum sealed before irradiation with bacon vacuum sealed after irradiation.

Using the recommended 16 oz. fill in the 303 x 509 can, the post-irradiation vacuum closing was effective in reducing radiation gas. Using a 20 oz. fill the post-irradiation vacuum closing technique was not sufficiently effective to prevent all cans from swelling. The higher fill interfered with gas removal in the short time available, and did not provide a reservoir for vacuum.

Although other gases did not change noticeably over the various examinations, CO_2 observed at 6 months storage had increased over previous values. This higher value for CO_2 was confirmed in a 307 x 409 can of bacon stored 21 months at 21°C data for which are presented in Table 14a. A simple test using hydrogen peroxide on this latter sample indicated catalase activity in the bacon.

None of a panel of five tasters reported typical radiation off flavor in the product stored 21 months. Two tasters reported the product definitely changed since earlier examinations, however, describing it as "unnaturally sweet" or "muddy". A layer of brownish liquid had settled in the bottom of the can, a phenomenon not previously noted with this product, and it was concluded that autolysis had been taking place.

Enzymatic changes have been reported with other irradiated meat products (Pratt and Ecklund, 1956) on extended storage and increased CO_2 identified in the headspace gas (Pratt, 1960, pages 13, 14).

(b) Beef

Table 15 shows the post-irradiation vacuum close for beef reduced radiation gas as expected.

Overshadowing the benefits of the post-irradiation close was the fact that this variable was closed cold while the pre-irradiation vacuum variables could be closed hot. The benefits of the warm closure so outweighed the benefits of the post-irradiation vacuum close that the former variable contained consistently less total gas.

A single can of beef evacuated and sealed after sterilization was found to be a hard swell. Bacteriological examination of the can revealed the product to have spoiled due to a mixed bacterial flora characteristic of recontamination. Pressure testing of this container plus detailed physical examination indicated the container and seams were not defective.

Although this single can represents an isolated case, it should serve as a reminder that the technique of sealing after irradiation may require special sanitary precautions to prevent recontamination.

(c) Pork

Gas analysis for pork irradiated in 401 x 209 cans at 4.5 Mrads is presented in Table 16.

(d) Ham

Table 17 reveals a modest reduction in total gas and in hydrogen using the post-irradiation vacuum closure.

(e) Chicken Breast

As with beef (Paragraph A 1 (b) above), other factors overshadowed the benefit of post-irradiation vacuum close although a consistent reduction in hydrogen was effected. See Table 18.

(f) Chicken thigh with bone in

Gas analysis for chicken thigh with bone in irradiated in 401 x 209 cans at 4.5 Mrads is presented in Table 19.

3. <u>Hydrogen permeable plastic window container</u>.

(a) Mylar Window

The specially constructed "Mylar" window cans returned from the irradiation source in a very pronounced swelled condition. Within a month so much hydrogen gas had diffused out that the end of the can

was tightly drawn in as by a good vacuum. Figure 3 demonstrates this condition with ham.

Gas analysis in Table 20 confirms the almost total diffusion of hydrogen out of the can by 6 months. Unfortunately it also demonstrates the gradual diffusion of oxygen into the can. Accordingly the Mylar window was considered too permeable to oxygen.

(b) Mylar/Saran Window

The ham irradiated in window cans showed the same rapid diffusion of hydrogen out of the can as shown in Table 21(a) to produce the effect shown in Figure 3.

Gas analysis in Table 21 confirms the total absence of hydrogen by 3 months. The appearance of the product was satisfactory and oxygen analysis was low. The very low analysis of oxygen in the headspace, however, hides the fact that oxygen passing through the film in small amounts may be reacting with the product. By twelve months, the appearance of the ham had changed seriously (probably due to oxidation) although headspace oxygen remained low.

4. <u>Palladium catalyst to reduce irradiation gas</u>.

(a) Dry Sucrose - High Pd

Table 22 reveals the rapid effect of 1 gm palladium in eliminating oxygen as well as radiation produced hydrogen. The principle was clearly demonstrated although palladium in this amount is expensive.

(b) Ham - Low Pd

Table 23 shows reduced hydrogen with 3 levels of added palladium. The mechanism here can be seen to be twofold.

(1) With small amounts of Pd there is effective catalyzation of oxidation of the hydrogen as long as oxygen is present.

(2) With large amounts of Pd there is an additional absorption of excess hydrogen over the above that which is oxidized.

(c) Ham in Pd Catalyzed Pouches

Table 24 shows analysis of gas from irradiated pouches of ham after 12 months. Those pouches incorporating very small amounts of palladium still effect some reduction in hydrogen.

Ham in
Plastic Window Can

Can Showing Internal
Pressure From Irradiation
Induced Gases

Formerly Swelled
Can 3 Weeks
After Irradiation

Table 25 shows no change in total gas as storage progresses from 2 weeks to six months.

(d) Shrimp in Pd Catalyzed Pouches

Table 26 shows analysis of gas from irradiated pouches of shrimp. A reduction of hydrogen gas is noted as with the ham above.

(e) Shrimp in Cans - Very Low Pd

As shown in Table 27 there was no reduction of total gas even after a year in hermetic cans with small amounts of palladium closed under high vacuum. This is because there was insufficient palladium to absorb any appreciable amount of hydrogen and too little oxygen for the catalytic effect to do any good.

Sources of Headspace Gas

Summarizing the sources of headspace gas described in this report, there are five:

1. Atmospheric gas trapped in the headspace - N_2 and O_2.
2. Radiation induced gas - H_2 (and some CH_4, CO and CO_2).
3. Gas produced by enzymatic activity on long storage - CO_2.
4. Gas produced by bacterial spoilage - CO_2.
5. Gas diffusing through plastic film - O_2.

T A B L E 1

IRRADIATION INDUCED GASES IN PACKAGED FOODS

T A B L E 1(a)

EXAMINATION OF STORED PRODUCTS

Canned samples remaining from previous irradiation tests; stored five to seven years.

Irrad. Dose - 4.5 to 5.6 Mrads
Can Size - 307 x 509
Storage - 5 - 7 Years

Product	Enzyme Activity	Total Headspace Gas (ml)	Gas Composition (%)						
			N_2	O_2	H_2	CO_2	CO	CH_4	H_2S
Chili	Inactive	39.6	4.6	0	85.5	5.3	1.7	2.6	0
Cherries	Inactive	22.0	3.9	0	86.0	8.2	1.8	0	0
Green Beans	Inactive	56.0	17.0	0	75.8	7.0	0	0.2	0
Ground Beef	Active	80.0	32.9	1.3	29.3	31.0	2.2	3.2	0
Ground Beef	Inactive	25.0	30.5	0.4	48.3	17.8	1.4	1.6	0

Note the relatively high CO_2 content in "enzyme active" beef; also the high total gas content as compared to "enzyme inactive" beef.

No H_2S detectable in any samples.

TABLE 1(b)

HEADSPACE GAS IN PACKAGED WHOLE BONED HAM

Irradiation Dose - 4.5 Mrads

Container	Storage Time	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
Polyethylene bag within a polyethylene bag	4 Months	80	87.7	9.0	0	0	1.6	1.7
Polyethylene/Al foil laminate within a polyethylene bag	4 Months	40	81.0	2.0	0.01	0	11.6	5.4
#10 Tinplate Can	79 Months	800	35.7	0	46.5	17.8	0	0.02

Note 1 - Above samples were submitted by U.S. Army Natick Laboratories; packaging procedures are not known.

Note 2 - Storage conditions are not known, but it is believed that samples were stored under ambient conditions.

T A B L E 2

HEADSPACE GAS IN MODEL SYSTEMS REPRESENTING INDIVIDUAL FOOD COMPONENTS

Three Months Storage at 21°C

Irradiation Dose - 4,5 Mrads
Can Size - 303 x 406

Model System	Treatment	Total Gas (ml)	N_2	O_2	H_2	CO_2	CO	CH_4
			Composition (%)					
Water (distilled)	Irrad.	5.0	37.0	1.1	58.7	3.3	0	0
Water + 2% NaCl	"	5.5	29.4	0	68.6	2.0	0	0
Water + 10% Sucrose	"	50.0	9.2	1.6	82.5	4.1	2.5	0
Water + 10% Starch	"	50.0	16.2	2.5	78.5	1.1	1.8	0
Water + 10% Dextrose	"	58.0	9.2	1.3	81.2	6.6	1.7	0
Water + 6% Gelatin	"	40.0	8.4	0	65.1	0.3	22.8	3.4
Water + 10% Corn Oil	"	15.0	17.5	0	79.4	0.4	2.4	0.3
Sucrose (Dry)	"	162	13.4	1.8	84.0	0	0	0
Starch (Dry)	"	170	8.8	0	71.6	4.8	14.9	0
Dextrose (Dry)	"	170	12.9	1.1	83.7	2.3	0	0
Gelatin (Dry)	"	45	86.2	6.8	1.2	0.1	2.5	3.3
Oil (Dry)	"	60	61.4	1.8	33.5	0	3.1	0.1

TABLE 3

HEADSPACE GAS IN MODEL SYSTEMS

Model System	Total Gas (ml)	Unirradiated Controls Percent % N_2	O_2	H_2	CO_2	CO	CH_4
Water (Distilled)	0.6	93.6	5.3	1.1	0	0	0
Water + 2% NaCl	0.3	93.0	5.6	1.5	0	0	0
Water + 10% Sucrose	0.9	96.2	3.2	0.6	0	0	0
Water + 10% Starch	2.2	91.1	2.0	0.3	5.6	1.1	0
Water + 10% Dextrose	1.9	28.6	0.7	2.2	68.4	0	0
Water + 6% Gelatin	1.8	94.2	3.9	2.0	0	0	0
Water + 10% Corn Oil	2.5	98.2	0.3	0.3	0	1.2	0
Sucrose (Dry)	12	79.4	20.5	0.1	0	0	0
Starch (Dry)	17	79.8	20.1	0.1	0	0	0
Dextrose (Dry)	11	79.8	20.1	0.1	0	0	0
Gelatin (Dry)	30	99.5	0.4	0.1	0	0	0
Oil (Dry)	25	80.5	19.5	0	0	0	0

TABLE 4

EFFECT OF IRRADIATION TEMPERATURE ON GAS PRODUCTION IN SUCROSE AND GELATIN SOLUTIONS

Irradiation Dose - 4.5 Mrads
Can Size - 303 x 406

Initial Examination

Total Headspace Gas (ml)

Irradiation Temperature	10% Sucrose Solutions	6% Gelatin Solution
20°C	58	35
5°C	62	32
-40°C	31	23
-80°C	29	23
-196°C	23	21
Control (Unirrad.)	5	4

4 Months at 21°C

	10% Sucrose Solution		6% Gelatin Solution	
	Total Gas (ml)	H_2 (ml)	Total Gas (ml)	H_2 (ml)
20 C	50	43	31	19.5
5 C	49	43	30	20.3
-40 C	30	25	30	3
-80 C	24	19.5	22	1.3
-196 C	31	15.5	6*	2.5*
Control (Unirrad.)				

* Cracked sideseams resulted in partial leakage of gas, hence low total gas value.

TABLE 5

EFFECT OF PACKAGING MATERIALS ON H_2 PRODUCTION IN 25% SUCROSE SOLUTION

Irradiation Dose - 4.5 Mrads

		H_2 (ml)	
Container	Treatment	Initial	3 Mo. @ 21°C
Tinplate 202 x 204	Irrad.	8.0	9.2
Tinplate 202 x 204	Not Irrad.	0	0.1
Glass	Irrad.	6.0	7.8
Glass	Not Irrad.	.06	.02
*Plastic (Inside of Pouch)	Irrad.	1.9	1.2
*Plastic (Outside of Pouch)	Irrad.	7.8	9.2
Plastic	Not Irrad.	0	0

*Plastic pouch contained in 202 x 204 tinplate can closed under full vacuum.

TABLE 6

THE EFFECT OF IRRADIATION DOSE AND SUCROSE CONCENTRATION ON GAS PRODUCTION

Model System	Irrad. Dose	Total Gas (ml)	Composition (%)					
			N_2	O_2	H_2	CO_2	CO	CH_4
1% Sucrose	0 Mrad	2.0	86.2	1.9	11.8	0	0	0
" "	2 Mrad	25.0	14.9	0	70.3	13.0	1.7	0
" "	4 Mrad	38.0	6.2	0	78.6	13.0	2.1	0
" "	8 Mrad	78.0	4.8	0	80.8	10.8	3.5	0
5% Sucrose	0 Mrad	2.0	95.5	2.3	1.3	0	0.9	0
" "	2 Mrad	25.0	7.1	0	80.3	10.4	2.3	0
" "	4 Mrad	30.0	2.8	0	86.5	8.3	2.4	0
" "	8 Mrad	85.0	1.8	0	86.6	8.3	3.3	0
25% Sucrose	0 Mrad	1.0	94.6	3.7	1.7	0	0	0
" "	2 Mrad	33.0	5.1	0	82.0	10.6	2.3	0
" "	4 Mrad	60.0	2.2	0	86.6	8.7	2.5	0
" "	8 Mrad	111.0	1.1	0	87.4	8.5	3.0	0

T A B L E 7

THE EFFECTS OF IRRADIATION DOSE AND GELATIN CONCENTRATION ON GAS PRODUCTION

Initial Examination (3 Months at 21°C)
Can Size 303 x 406

Model System	Irrad. Dose	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
1% Gelatin	2 Mrad	15.0	12.0	0	81.5	2.1	2.2	2.2
" "	4 Mrad	25.0	7.5	0	86.6	2.1	1.4	2.4
" "	8 Mrad	28.0	7.8	0	88.8	2.1	0	1.2
6% Gelatin	0 Mrad	1.5	83.5	4.7	6.9	0	0	0
" "	2 Mrad	12.0	18.1	0.6	54.9	2.2	21.0	3.2
" "	4 Mrad	30.0	10.2	0.3	62.9	4.3	18.9	3.4
" "	8 Mrad	60.0	3.9	0	71.4	2.1	19.4	3.2
12% Gelatin	0 Mrad	1.5	88.6	5.3	4.2	0	1.5	0.4
" "	2 Mrad	14.0	18.5	1.2	43.0	4.3	30.1	2.9
" "	4 Mrad	30.0	13.5	0.4	51.1	2.2	29.6	3.2
" "	8 Mrad	60.0	6.1	0.3	57.4	2.2	30.7	3.3

T A B L E 8

GAS PRODUCED ON IRRADIATION OF SIMULATED FOODS

Irradiation Dose - 4.5 Mrads
Can Size - 303 x 406

Initial Examination

Food Type	Treatment	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
High-carbohydrate	Irrad.	41.5	5	0	81	4	3	1
	Unirrad. (Control)	3.5	99	1	0	0	0	0
High-protein	Irrad.	31.7	19	0	52	7	20	2
	Unirrad. (Control)	5.6	92	1	3	3	0	0

3 Months @ 21°C

Food Type	Treatment	Total Gas (ml)	N_2	O_2	H_2	CO_2	CO	CH_4
High-carbohydrate	Irrad.	44.0	5.2	0	87.3	3.8	3.2	0.5
	Not Irrad.	3.5	99	0.8	0.2	0	0	0
High-protein	Irrad.	40.0	18.5	0	50.5	7.2	19.3	1.7
	Not Irrad.	5.6	91.0	1.8	3.6	3.6	0	0

TABLE 9

VOLUME OF GAS PRODUCED IN VARIOUS PACKAGED MEAT PRODUCTS IRRADIATED AT 4.5 MRADS

Product	Vol. (ml) of Gas*/lb. of Product: Estimated**	Measured: 1 Mo.	Measured: 3 Mo.	Measured: 6 Mo.
Beef	32	31,33	35,30,33	
Pork	36	36,44	36,34,33	
Chicken Breast (Boneless)	33	30,32	32,32,32	
Chicken Thigh (With Bone)	29	28,29	23,28,26	
Ham	37	37,40	36,30,35	
Bacon (16 Oz. fill in 303 x 509 can)	32	30,32	35,37	31,31,35
***Bacon (20 oz. fill in 303 x 509 can)	40	22,18, 26	24,25	21,21,21

* Includes H_2, CH_4, CO and CO_2

** Based on Proximate Analysis of the product

*** Lower gas volume in overfilled (20 oz.) can probably due to incomplete removal of gas from the meat tissues.

TABLE 10

EFFECT OF CLOSING VACUUM ON GAS PRODUCTION IN CANNED CHICKEN BREASTS

Can Size - 404 x 700
Irradiation Dose - 4.5 Mrads

Initial Closing Vacuum (in. Hg)	Total Gas (ml) Init.	6 Mo.	12 Mo.	Initial Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
10	280	320	370	71.7	0.1	16.5	6.4	4.2	1.3
15	240	230	268	66.6	0.2	20.7	6.4	4.8	1.5
20	189	205	*	58.3	0.2	24.9	8.7	6.2	1.7
25	140	140	150	48.1	0.3	31.0	11.1	7.4	2.1

Initial Closing Vacuum (Inch Hg)	Irradiation Gas H_2, CO_2, CO, CH_4 ml (Initial)
10	80
15	80
20	75
25	72

* Gas lost during sampling

TABLE 11

EFFECT OF pH ON GAS PRODUCTION IN 6% SUCROSE SOLUTIONS IRRADIATED AT 4.5 MRADS

pH (Initial)	pH (After) (Irrad.)	Total Gas (ml)	N_2 (ml)	O_2 (ml)	H_2 (ml)	CH_4 (ml)	CO (ml)	CO_2 (ml)
6.8	7.1	41.9	2.4	0	38.8	0	.8	0
6.8	7.1	42.0	3.0	0	36.3	0	.7	2.1
6.8 (Control)	-	2.8	2.0	0	0.2	0	0	0.3
5.5	5.9	47.0	2.9	0	39.9	0	.9	3.4
5.5	5.9	50.0	3.2	0	41.4	0	.7	4.7
5.5 (Control)	-	2.8	2.3	0.1	0.3	0	0	0.2
4.0	4.4	60	1.3	0	54.4	0	.6	3.7
4.0	4.4	60	1.7	0	53.3	0	.6	4.4
4.0 (Control)	-	2.2	1.3	0	0.9	0	0	0

TABLE 12

THE EFFECTS OF RADIATION SOURCE AND TEMPERATURE ON RADIATION INDUCED GAS IN BEEF PACKED IN FLEXIBLE PACKAGES

Radiation Temp (°C)	Radiation[1] Source	Radiation[2] Gas (ml)	Composition (%)[3] H_2	CO_2	CO	CH_4
25	Co 60	4.5	73.7	15.9	5.5	4.6
0	Co 60	3.6	78.8	15.8	0.4	5.0
-80	Co 60	2.4	48.3	45.2	0	6.5
-80	Electron	1.1	73.0	23.0	0	4.0
0	Electron	3.6	68.5	22.4	0	4.2
25	Electron	4.8	72.5	21.3	2.6	3.7

1 Co 60 radiation dose 4.5-5.6 Mrad
Electron radiation dose 4.5 Mrad

2 Total Headspace gas less N_2 and O_2

3 Composition by % of radiation gas

T A B L E 13

RECOMMENDED FILLS (OZ. AV.) TO PRODUCE 10 IN. Hg CAN VACUUM AFTER 4.5 MRAD IRRADIATION

Can Size	Product	Closing Vac. - 15"	Fill (Oz. Av.) 20"	25"	28"
401 x 209	Bacon or Beef	10.6	12.5	13.2	13.5
	Pork	10.2	12.2	13.0	13.3
	Chicken	10.5	12.4	13.2	13.5
	Ham	10.1	12.1	13.0	13.3
303 x 509	Bacon or Beef	15.4	18.1	19.2	19.6
	Pork	14.8	17.7	18.9	19.3
	Chicken	15.2	18.0	19.1	19.5
	Ham	14.7	17.7	18.8	19.3
404 x 700	Bacon or Beef	36.3	42.6	45.3	46.2
	Pork	35.0	41.7	44.6	45.6
	Chicken	35.9	42.4	45.1	46.0
	Ham	34.7	41.5	44.4	45.4
603 x 700	Bacon or Beef	76.9	90.3	95.9	97.9
	Pork	74.1	88.4	94.4	96.6
	Chicken	76.2	89.9	95.5	97.6
	Ham	73.5	87.9	94.1	96.3

T A B L E 14

POST IRRADIATION VACUUM CLOSURE
RADIATION INDUCED GAS IN BACON

Irradiation Dose - 4.5 Mrads
Can Size - 303 x 509

Fill	Sealed	Storage (°C)	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
16 oz.	Before Irrad.	Initial	80	55.6	0.2	37.3	2.8	3.1	0.7
		4 Mo.	92	55.6	0.2	36.0	5.6	2.3	0.5
		6 Mo.	87	54.4	0.5	34.2	7.8	2.6	0.5
		16 Mo.	82	56.7	0.7	35.1	4.2	2.7	0.6
16 oz.	After Irrad.	Initial	50	54.9	0.6	34.5	5.7	3.5	0.8
		4 Mo.	60	56.0	1.2	31.8	7.6	2.8	0.6
		6 Mo.	55	63.0	0.4	26.1	7.3	2.7	0.6
		16 Mo.	59	54.9	0.5	29.1	12.1	2.8	0.6
16 oz.	Frozen	Initial	67	86.0	11.7	0	2.3	0	0
		4 Mo.	-	-	-	-	-	-	-
		6 Mo.	56	85.5	14.5	0	0	0	0
		16 Mo.	55	86.0	1.8	0	12.2	0	0
20 oz.	Before Irrad.	Initial	50	44.1	0.2	49.3	2.3	3.6	0.6
		4 Mo.	56	40.4	0.1	50.9	5.2	3.1	0.5
		6 Mo.	52	43.6	0.9	45.6	6.6	2.8	0.5
		16 Mo.	59	42.0	0.3	45.0	9.1	3.1	0.5
20 oz.	After Irrad.	Initial	53	37.8	0.1	52.6	5.1	3.9	0.6
		4 Mo.	42	39.6	0.2	53.1	2.6	3.9	0.5
		6 Mo.	47	43.3	0.7	48.8	6.5	3.2	0.5
		16 Mo.	47	37.6	0.4	53.1	5.6	3.0	0.4
20 oz.	Frozen	Initial	25	90.4	7.4	0	2.3	0	0
		4 Mo.	-	-	-	-	-	-	-
		6 Mo.	27	95.9	4.1	0	0	0	0
		16 Mo.	35	88.8	0.5	0	10.8	0	0

TABLE 14(a)

HEADSPACE GAS IN IRRADIATED CANNED BACON
STORED 21 MONTHS @ 21°C

Irradiation Dose - 4.5 Mrads
Can Size - 307 x 509

		Gas Volume (ml)						
Product	Fill (Oz. Av.)	N_2	O_2	H_2	CH_4	CO	CO_2	Total
Bacon	21	19.1	0.1	38.9	0.5	2.4	7.0	68

T A B L E 15

POST IRRADIATION VACUUM CLOSURE
RADIATION INDUCED GAS IN PRECOOKED BONELESS BEEF LOINS

Irradiation Dose - 4.5 Mrads
Can Size - 401 x 209

Irradiation Temp (°C)	Container Sealed	Storage at 70°C (mos)	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
2°C	Before Irrad.	2	38	36.0	0.4	43.2	18.2	0	2.2
-185°C	Before Irrad.	2	38	47.7	0.4	29.0	22.5	0	0.5
2°C	After Irrad.	2	52	74.0	0.4	16.5	8.0	0	1.1
-185°C	After Irrad.	2	66	72.1	3.8	12.2	11.9	0	0.1
2°C	Not Irrad.	2	50	78.5	19.0	0	2.6	0	0
-185°C	Not Irrad.	2	50	78.5	18.9	0	2.6	0	0
2°C	Before Irrad.	6	42	40.1	0.4	39.0	18.5	0	2.0
-185°C	Before Irrad.	6	37	54.1	0.2	29.0	16.2	0	0.6
2°C	After Irrad.	6	50	68.4	0.2	21.9	8.4	0	1.1
-185°C	After Irrad.	6	59	77.0	0.2	13.8	8.8	0	0.2
-185°C	Not Irrad.	6	50	89.0	8.3	0	2.8	0	0
2°C	Before Irrad.	12	43	40.0	0.1	43.5	14.6	0	1.9
-185°C	Before Irrad.	12	32	41.3	0.3	30.2	27.5	0	0.7
2°C	After Irrad.	12	50	73.3	0.3	20.4	4.4	0.3	1.3
-185°C	After Irrad.	12	61	75.3	0.1	17.9	6.6	0	0.1

TABLE 16

RADIATION INDUCED GAS IN PRECOOKED PORK LOINS

Irradiation Dose - 4.5 Mrads
Can Size - 401 x 209

Irradiation Temp (°C)	Container Sealed	Storage at 21°C (Mos)	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
2°C	Before Irrad.	2	59	45.2	0.2	37.6	13.3	2.4	1.2
-	Not Irrad.	2	43	77.5	17.3	0	5.3	0	0
2°C	Before Irrad.	6	53	47.3	0	38.0	11.9	1.7	1.1
-	Not Irrad.	6	-	-	-	-	-	-	-
2°C	Before Irrad.	12	54	46.1	0.1	38.2	10.8	3.3	1.5

TABLE 17

POST IRRADIATION VACUUM CLOSE
IRRADIATION INDUCED GAS IN SMOKED BONELESS HAM

Irradiation Dose - 4.5 Mrad
Can Size - 401 x 509

Irradiation Temp (°C)	Can Sealed	Storage at 21°C (Mos)	Total Gas (ml)	Composition (%)					
				N_2	O_2	H_2	CO_2	CO	CH_4
2°C	Before	2	68	51.5	0.1	32.2	11.9	2.5	1.7
2°C	After	2	64	58.0	0.3	24.3	13.3	2.4	1.7
-	Not Irrad.	2	42	78.7	18.6	0	2.6	0	0
2°C	Before	6	66	52.6	0.1	29.4	14.5	1.9	1.4
2°C	After	6	60	59.9	0.1	25.8	10.1	2.6	1.5
-	Not Irrad.	6	47	77.3	9.9	0	12.8	0	0
2°C	Before	12	68	53.7	0.1	32.4	8.9	2.8	1.8
2°C	After	12	50	56.1	0.6	24.8	13.3	3.5	1.5

T A B L E 18

POST IRRADIATION VACUUM CLOSURE
IRRADIATION INDUCED GAS IN PRECOOKED BONELESS CHICKEN BREASTS

Irradiation Dose - 4.5 Mrads
Can Size - 401 x 209

Irradiation Temp (°C)	Container Sealed	Storage at 21°C (Mos)	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
2°C	Before	2	31	19.8	0.4	57.1	12.8	7.0	2.9
-185°C	Before	2	23	48.9	0.7	36.0	13.3	0	0.9
2°C	After	2	47	73.1	0.4	15.9	5.9	3.3	1.4
2°C	Not Irrad.	2	54	91.5	5.8	0	2.7	0	0
-185°C	Not Irrad.	2	32	91.4	3.3	0	5.3	0	0
2°C	Before	6	39	33.4	1.0	47.2	12.1	4.9	1.8
-185°C	Before	6	20	44.2	0.6	41.1	13.0	0	1.0
2°C	After	6	43	75.7	0.3	11.4	7.8	3.4	1.4
2°C	Not Irrad.	6	30	95.2	0.9	0	3.9	0	0
2°C	Before	12	33	26.1	0.7	55.7	8.2	6.8	2.5
-185°C	Before	12	25	55.4	0.7	31.3	11.7	0	0.9
2°C	After	12	45	72.8	0.3	15.5	6.5	3.5	1.4

TABLE 19

RADIATION INDUCED GAS IN CHICKEN THIGH (BONE IN)

Irradiation Dose - 4.5 Mrad
Can Size -401 x 209

Irradiation Temp (°C)	Can Sealed	Storage at 21°C (Mos)	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
2°C	Before	2	43	39.6	0.3	42.3	13.9	1.8	1.9
-	Not Irrad.	2	107	84.8	9.9	0	5.3	0	0
2°C	Before	6	40	35.0	0.1	44.6	16.3	2.0	2.1
-	Not Irrad.	6	100	92.0	1.6	0	6.4	0	0
2°C	Before	12	45	42.7	0.8	36.9	14.1	1.6	1.9

TABLE 20

IRRADIATION INDUCED GAS IN DRY SUCROSE IN "MYLAR" WINDOW CANS

Irradiation Dose - 4.5 Mrads
Can Size - 404 x 307

Treatment	Storage at 21°C (Mos)	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
Irradiated	3	260	64.7	17.6	15.1	0	0	0
Non-Irradiated	3	235	78.7	21.3	0	0	0	0
Irradiated	6	258	78.1	21.1	0.8	0	0	0
Non-Irradiated	6	258	78.7	21.3	0	0	0	0

T A B L E   21

IRRADIATION INDUCED GAS IN SMOKED BONELESS HAM IN MYLAR/SARAN WINDOW CANS

Irradiation Dose - 4.5 Mrads
Can Size - 401 x 209

Treatment	Storage at 21°C (Mos)	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
Irradiated	1	40	69.8	0.6	9.4	11.7	5.7	2.8
Not Irradiated (Frozen at -20°C)	1	20	94.3	0.5	0	5.3	0	0
Irradiated	3	51	77.1	0.1	0	16.1	4.2	2.4
Not Irradiated (Frozen at -20°C)	3	12	97.1	0.4	0	2.5	0.	0
Irradiated	12	21	71.9	0.4	0	16.5	7.6	3.9
Not Irradiated (Frozen at -20°C)	12	15	91.0	0.3	0	8.6	0	0

T A B L E   21(a)

IRRADIATION INDUCED GAS IN SMOKED BONELESS HAM IN MYLAR/SARAN WINDOW CANS

Sample No.	Container Freespace (ml)* 2 Weeks	5 Months	8 Months
1	50	-	-
2	50	39	39
3	85	-	-
4	62	-	-
5	23	14	14
6	22	15	15
7	23	-	-
8	35	-	-
9	17	12	12
10	58	-	-
11	34	27	27
12	24	18	17

*Measured by the technique of weighing under water

T A B L E 22

EFFECT OF PALLADIUM ON RADIATION INDUCED HEADSPACE GAS IN DRY SUCROSE

Irradiation Dose - 4.5-5.9 Mrads
Can Size - 303 x 406

Variable	Treatment	Storage at 21°C (Mos)	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
Sucrose + 1 gm Pd	Irrad.	1	170	91	7	0.1	1.8	0	0
Sucrose (No Pd)	Irrad.	1	257	60	15	25.0	0	0	0
Sucrose + 1 gm Pd	Not Irrad.	1	202	79	21	0	0	0	0
Sucrose + 1 gm Pd	Irrad.	6	170	99.5	0.4	0.1	0	0	0
Sucrose (No Pd)	Irrad.	6	267	60.0	15.0	25.0	0	0	0
Sucrose + 1 gm Pd	Not Irrad.	6	220	79.0	21.0	0	0	0	0

TABLE 23

EFFECT OF PALLADIUM ON RADIATION INDUCED HEADSPACE GAS IN CANNED BONELESS ROLLED HAM

Irradiation Dose - 4.5 - 5.9 Mrads
Can Size - 401 x 209
Storage Temp. - 22°C

Palladium Addition (mg)	Treatment	Storage (Mos)	Total Gas (ml)	Composition (%)					
				N_2	O_2	H_2	CO_2	CO	CH_4
0.5	Irrad.	2	55	56	1.2	30.4	9.5	1.6	1.2
5.0	Irrad.	2	56	60	1.1	27.0	8.0	2.5	1.6
50.0	Irrad.	2	42	76	0.7	9.8	11.5	0	2.2
0	Irrad.	2	67	55	0.6	33.0	7.5	2.7	1.4
0	Frozen	2	41	78	20.5	0	1.4	0	0
0.5	Frozen	2	37	77	20.6	0	2.7	0	0
0.5	Irrad.	12	60	57.2	0.1	32.2	6.7	2.4	1.5
5.0	Irrad.	12	55	57.8	0.1	28.5	9.1	2.8	1.8
50.0	Irrad.	12	42	78.2	0.5	8.2	9.9	0	3.2
0	Irrad.	12	70	53.5	0.4	34.1	8.2	2.4	1.4
0	Frozen	12	46	83.0	13.8	0	3.2	0	0
0.5	Frozen	12	46	84.0	12.3	0	3.7	0	0

TABLE 24

EFFECT OF PALLADIUM ON RADIATION INDUCED HEADSPACE GAS IN BONELESS ROLLED HAM PACKED IN LAMINATED FLEXIBLE PACKAGES

Irradiation Dose -4.5-5.6 Mrads
Storage - 12 Months

Package Type	Sealing Vacuum (in Hg)	Treatment	Total Gas (ml)	Composition (%)					
				N_2	O_2	H_2	CO_2	CO	CH_4
Pd Catalyzed[1]	28	Irrad.	4	65.3	0.8	23.2	0	8.4	2.4
Pd Catalyzed	0	Irrad.	24	81.8	0.1	10.5	4.8	1.9	1.0
Pd Catalyzed	28	Frozen	3	96.9	3.1	0	0	0	0
No Pd[2]	28	Irrad.	7	29.3	0	52.3	10.0	6.0	2.4
No Pd	0	Irrad.	33	68.2	0	19.0	10.4	1.7	0.8
No Pd	28	Frozen	0.5	97.4	2.6	0	0	0	0
No Pd	0	Frozen	26	82.0	14.7	3.3	0	0	0

[1] Catalyzed pouch - 5" x 5" laminated from inside out with polyethylene/Pd catalyst*/polyethylene/aluminum foil/paper.

* Pd deposited on Aluminum

[2] Non catalyzed (standard) pouch - 3" x 7" laminated from inside out with polyethylene/aluminum foil/mylar.

TABLE 25

EFFECT OF PALLADIUM ON HEADSPACE GAS
IN LAMINATED POUCHES PACKED WITH HAM

Irradiation Dose - 4.5 Mrads

Pouch Variable	Sealing Vacuum (ins.Hg)	Freespace (ml)* 2 Wks. (21°C)	2 Months (21°C)	6 Months (21°C)
With Pd.**	28	8	8	6
No Pd.	28	9	9	8
With Pd	0	28	28	27
No Pd.	0	32	32	32
No Pd.-Frozen (Not Irrad.)	28	0		0

* Measured by the technique of weighing under water; average of 4 samples per variable.

** Approximately 0.3 mg. Pd. per pouch.

TABLE 26

EFFECT OF PALLADIUM ON RADIATION INDUCED GAS IN SHRIMP PACKED IN FLEXIBLE PACKAGES

Package Type	Storage at 22°C (Mos)	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	CO	CH_4
Pd Catalyzed	1	1.4	89.1	3.7	6.5	0	0	0.7
No Pd	1	3.8	67.5	1.0	27.7	1.8	0	2.0
Pd Catalyzed	12	0.5	88.2	11.8	0.04	0	0	0
No Pd	12	3.0	89.5	1.8	3.9	2.8	0	2.1

TABLE 27

EFFECT OF PALLADIUM ON RADIATION
INDUCED GAS IN SHRIMP PACKED IN #2-1/2 CANS

Irradiation Dose-4.5-5.6 Mrads

Palladium	Storage (Mos)	Total Gas (ml)	Composition (%) N_2	O_2	H_2	CO_2	COO	CH_4
0.5 mg	1	77	90.8	0.8	2.7	5.2	0	0.4
0	1	64	87.2	1.1	6.5	4.5	0	0.6
0.5 mg	12	86	87.6	1.3	4.1	6.5	0	0.5
0	12	86	86.2	0.9	5.7	6.6	0	0.6

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